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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US89/02056 (22) International Filing Date: 12 May 1989 (12.05.89) (30) Priority data: 193,805 13 May 1988 (13.05.88) US (60) Parent Application or Grant (63) Related by Continuation US 193,805 (CIP) Filed on 13 May 1988 (13.05.88) (71) Applicant (for all designated States except US): ADVANCED POLYMER SYSTEMS, INC. [US/US]; 2800 High Ridge Road, Boynton Beach, FL 33426 (US). (72) Inventor; and (75) Inventor/Applicant (for US only) : WEIDMAN, Larry, G. [US/US]; 15730 Glendale Lane, Fort Myers, FL 33912 (US).		(74) Agent: COLLINS, John, M.; Hovey, Williams, Timmons & Collins, 1400 Mercantile Bank Tower, 1101 Walnut Street, Kansas City, MO 64106-2165 (US). (81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE, DE (European patent), DK, FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), HU, IT (Eu- ropean patent), JP, KP, KR, LK, LU, LU (European pa- tent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: PROTECTIVE COATING FOR BOAT HULLS AND METHOD OF APPLYING THE SAME (57) Abstract <p>An improved, environmentally safe protective coating for marine surfaces is provided which is specially formulated for application to boat hulls for resisting marine growth thereon while minimizing release of toxic antifoulants into the environment. The coatings of the invention can therefore be used on boat hulls for preventing marine growth without the severe pollution effects associated with conventional antifoulant paints. The coatings are preferably made from powdered mixtures which include respective quantities of a polyamide such as Nylon 11, and a metallic antifoulant. In certain cases, the compositions may include an inorganic porous carrier such as carbon black, as well as glass spheres. In particularly preferred embodiments, use is made of an antifoulant such as elemental tin or copper or mixtures thereof together with an adhesive and an algicide. Application of the mixture to marine surfaces involves providing a supersonic gas stream, passing the gas stream through an electric arc thereby heating the gas stream and converting a portion thereof to plasma, injecting a quantity of the powdered mixture into the heated gas stream substantially downstream from the arc so as to melt the powder without overheating it, and then spraying the melted mixture onto a surface whereupon it cools and provides a bonded protective coating thereon.</p>		

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PROTECTIVE COATING FOR BOAT
HULLS AND METHOD OF APPLYING THE SAME

This is a Continuation-in-Part of identically titled application Serial No. 07/193,805 filed May 13, 1988.

Background of the Invention

1. Field of the Invention

The present invention is broadly concerned with a novel antifoulant coating for marine surfaces and a novel method for applying the coating to such surfaces. More particularly, it is concerned with a polyamide coating for boat hulls which in one embodiment preferably includes Nylon 11, carbon black and tributyltin fluoride for purposes of yielding a long lasting, marine growth resistant, environmentally safe coating for boat hulls. In other embodiments, the compositions of the invention advantageously includes a predominant amount of elemental copper or tin, together with a nylon terpolymer adhesive, an algicide and Nylon 11. The compositions are applied to provide a marine growth-resistant coating to a boat hull by providing an electric arc, directing a gas stream through the arc thereby heating the gas stream, injecting the powdered composition into the heated gas stream at a location downstream from the arc so as to melt the powder without overheating the same, and then applying the melted mixture to the surface to be coated.

2. Description of the Prior Art

Traditionally, high friction, abradable paints containing significant levels of antifoulants

1 have been applied to boat hulls to prevent marine
growth thereon. Such paints sometimes contain in
5 excess of 50% by weight of toxic antifoulants which
leach to the surface of the paint, thereby retarding
the formation of marine growths thereon. These
conventional paints are also designed to gradually
wear away as they are subjected to frictional forces
10 encountered as the boat moves through water. This
wearing away due to abrasion facilitates the gradual
removal of marine growth from the boat and thereby
continuously provides a new and growth-free paint
surface on the boat hull.

Typical paint application techniques
involve compressed air spraying of liquid paints
15 onto prepared boat hull surfaces. Preparation
usually involves cleaning of the hull surfaces, and
in the case of surfaces which are being repainted,
sanding or sandblasting is usually required in order
to remove the old paint prior to repainting.

20 These traditional paints and paint appli-
cation techniques have a number of problems or
shortcomings. Abradable paints containing high
levels of toxic, tin-based antifoulants result in
substantial environmental pollution due to the
25 direct and rapid release of large quantities of
these antifoulants into the water. The environmen-
tal impact of these paints is intensified by the loss
of tin containing paint particles into the water as
a result of abrasion. Accumulation of tin in shal-
low waters can and does kill and deform fish and
30 other marine life and may ultimately pose a hazard
to human consumers of seafood. Furthermore, tin-
based antifoulants have been used on aluminum boats
to the exclusion of copper based antifoulants due in

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1 part to a corrosive reaction between copper and
aluminum which can cause extensive damage to alumi-
num surfaces. Additionally, boats coated with
5 conventional paints must be occasionally blasted
with high pressure water spray, which adversely
affects the adherence of the paint to the hull, in
order to remove built up deposits such as scale.
Another shortcoming of many of these paints is that
10 they are relatively shortlived, quickly becoming
ineffective due to their tendency to rapidly leach
their antifoulants and their propensity to experi-
ence substantial wear during use of the boat. As a
consequence, conventional paints typically require
15 relatively frequent removal and replacement. Remov-
al of the old paint by techniques such as sanding
and sandblasting can create substantial quantities
of toxic paint dust which when inhaled can cause
serious illness and when washed into surrounding
20 waters can pollute the marine environment. Further-
more, conventional spraying techniques typically
result in substantial paint overspray and misting
which likewise can cause serious illness if inhaled.

Consequently, a need exists for improve-
ment in antifoulant, protective coatings for marine
25 surfaces which will result in reduced environmental
pollution while at the same time providing a low
maintenance, wear-resistant, protective coating
which resists marine growth.

Summary of the Invention

30 The problems outlined above are in large
measure solved by the present invention which pro-
vides an improved, long-lived, non-abrading, dense
coating for marine surfaces which is particularly
designed to be applied to marine surfaces such as

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1 boat hulls, submarine hulls, and propellers, for
purposes of preventing marine growth from forming
thereon while minimizing environmental pollution and
5 health hazards resulting from the coating. Broadly
speaking, in one aspect of the invention, the coat-
ing composition comprises respective amounts of a
polyamide in the nature of Nylon 10 or 11, an anti-
foulant, and preferably also an inorganic porous
10 carrier for the antifoulant. These ingredients are
selected and mixed so that the composition, when
applied to a marine surface, will provide a marine
growth resistant coating which is low friction, long
lasting, wear-resistant and relatively environmen-
15 tally safe. Advantageously, this resultant pro-
tective coating has an antifoulant release rate of
less than 5 micrograms per square millimeter per day
so as to minimize environmental pollution while at
the same time maintaining a protective coating
20 against marine growth. Therefore, the composition
of the invention can be used to good effect in
protecting boat hulls while providing a surface
coating which experiences reduced wear, extended
life, and reduced environmental impact.

Additionally, the present invention con-
25 templates the application of tin- or copper-based
antifoulants to aluminum boats by first coating the
hull of the boat with a dense, protective precoat
preferably about five to ten thousandths of an inch
thick of Nylon 10 or Nylon 11 and then applying
the antifoulant coating of the present invention
30 thereon.

In particularly preferred forms, the
composition of the invention includes Nylon 11,
carbon black, and tributyltin fluoride antifoulant.
However, other forms of nylon (e.g. Nylon 10) as
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1 well as other antifoulants (e.g., cuprous oxide and
bis-tributyltin adipate, $C_{30}H_{62}O_4Sn$) find utility in
the invention. Porous inorganic powdered substitutes
5 of carbon black which serve as a carrier for the
antifoulant (e.g., perlite, zinc oxide, various
paint clays and pigments) also can be used in the
invention. In yet another form, the composition of
the invention may include a portion of SiO_2 glass
10 spheres. The glass spheres do not melt when com-
bined and sprayed with the polyamide coating as
disclosed herein and imbed in the antifoulant
coating to increase the strength and abrasion resis-
tance of the antifoulant coating hereof.

In other preferred compositions, elemental
15 tin or copper in particulate form (49 microns or
less) is employed in substantial amounts ranging
from about 72% by weight up to an amount which would
render the composition effectively electrically
conductive, in combination with a polyamide such as
20 Nylon 10, Nylon 11 or mixtures thereof. In prac-
tice, the particulate, elemental tin or copper is
provided at a level of from about 72-82% by weight.
Such compositions further normally include from
about 4-8% by weight of a nylon terpolymer adhesive,
25 about 4-8% algicide, with the balance being a poly-
amide such as Nylon 11.

In coating application techniques, the
powdered compositions of the invention may be
injected into a high velocity, heated, plasma gas
stream which converts the powdered compositions to a
30 molten state and imparts a high velocity thereto.
The molten compositions and associated gas are then
directed into substantially one direction thereby
reducing any tendency of the molten compositions to
overspray or mist. The molten compositions are di-

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1 rect d at a prepar d marin surfac , whereupon they
cool and bond with the marine surface. High velo-
city impact of the molten compositions onto the
5 marine surface increases the bond strength there-
between. The resultant bonded polyamide coating is
wear-resistant, contains relatively small amounts of
antifoulant and leaches the antifoulant relatively
slowly, but at a rate sufficient to retard marine
10 growth thereon. Prior techniques and structures for
the application of polyamides or epoxy resins by
plasma spray are set out in U.S. Patents No.
3,851,140 and 4,049,842.

In addition to the aforementioned advan-
tages, the coatings hereof have relatively low
15 coefficients of friction and as a result will reduce
the noise, drag and energy needs of the boat as it
moves through the water. Subsequent coatings can be
applied onto the existing coatings without a sub-
stantial sacrifice in the bond strength of the
20 resultant coatings. Thus, new coatings can be
applied without necessitating the removal of pre-
vious, exhausted coatings. One additional aspect of
the present invention is that the total antifoulant
content of the coatings can be reduced by applying
25 antifoulant-free Nylon 11 undercoats prior to apply-
ing an outer antifoulant-containing final coat.

In addition, the present invention contem-
plates providing a skid-proof coating by combining
and jointly plasma spraying a friction enhancing
agent such as particles of aluminum oxide along with
30 Nylon 11 and/or the antifoulant composition of the
present invention.

The protective coatings disclosed herein
may be applied using the apparatus shown in my U.S.

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1 Application Serial No. 07/193,739 filed May 13,
1988, and such application entitled Apparatus and
Method for Applying Plasma Flame Sprayed Polymers,
5 which is incorporated herein by reference.

Description of the Preferred Embodiments

One preferred polyamide coating in accordance with the present invention includes about 82%
10 by weight of Nylon 11, about 6% by weight of carbon black, and about 12% by weight of tributyltin fluoride. This composition is initially in the form of a powdered mixture and is subsequently melted for application to a marine surface whereupon it cools and forms a dense, impact resistant coating.

15 In its broader aspects, this embodiment of the invention comprehends coating compositions having from about 62.5 to 82% by weight of polyamide selected from the group consisting of Nylon 10, Nylon 11 and combinations thereof, and more preferably
20 from about 70 to 82% by weight thereof; from about 25 to 60% by weight antifoulant such as tin or copper-based antifoulant materials, and preferably from about 25 to 37% by weight thereof; and from about 6 to 12% by weight porous inorganic carrier powder selected from the group consisting of carbon
25 black, zinc oxide and perlite, and more preferably from about 8 to 12% thereof.

Nylon 11, also known as poly[imino (1-oxo-1, 11-undecanediyl)], is a polyamide having the
30 chemical formula $H[HN-(CH_2)_{10}-CO]_nOH$ where n is approximately 50. The present invention also contemplates using various other forms of poly[imino (1-oxo-1, 11-undecanediyl)] including those where n is from 25 to 100. Nylon 11 can be obtained by the

1 self condensation of w-amino undecanoic acid or can
be obtained as a condensate of hexamethylene diamine
and w-amino undecanoic acid. This polyamide comes
5 in various grades of powder, has a melting point of
184 to 186°C, a bulk density of approximately .4 to
.5 and a true density at 20°C of approximately 1.04
to 1.12. Nylon 11 is available commercially, and in
actual practice may be obtained from Atochem, Inc.
10 of Glenrock, New Jersey, under the trade name Rilsan.
Nylon 10 is a powdered, polyamide having the
chemical formula $H[HN-(CH_2)_9-CO]_nOH$ where n is
preferably from about 25 to 100 and more preferably
about 50. Nylon 10 is also available commercially.

15 Tributyltin fluoride is an antifoulant
having a chemical formula $(C_4H_9)_3SnF$. Tributyltin
fluoride has a specific gravity of 1.27, and a
molecular weight of 309.39, a solubility in water of
.029 grams per liter and at room temperature is a
white powder having a characteristic odor. Tribu-
20 tyltin fluoride is available commercially, and in
actual practice may be obtained from M & T Chemi-
cals, Inc. of Rahway, New Jersey.

Another suitable antifoulant contemplated
by the present invention is cuprous oxide having the
25 formula Cu_2O . Cuprous oxide, also known as copper
oxide red, is in the form of reddish brown, octahe-
dral crystals which are insoluble in water, have a
density of 5.75 to 6.09, and a melting point of
1,235°C. Cuprous oxide is available commercially,
and in actual practice may be obtained from American
30 Chemet Corporation.

Carbon black is a porous inorganic powder
and in the present invention is used to increase the
amount of antifoulant which can be carried by the

1 polyamide and to increase the rate of leaching of
the antifoulant from the polyamide. Carbon black,
due to its porosity, serves to both carry the anti-
foulant and increase the porosity of the polyamide.
5 Carbon black also serves to prevent powdered tribu-
tyltin flouride from "balling up" thereby enhancing
the flowability of the premelt powdered mixture. A
usable form of carbon black is gas black which is a
fluffy black pigment produced by incomplete com-
bustion of natural gas. Another usable form of
10 carbon black is furnace black which is a finely
divided form of carbon made by burning vapor and
heavy oil fraction in a furnace at 50% of the air
required to complete combustion. Other forms of
15 carbon black also find utility. The preferred
carbon black product is purchased from Union Car-
bide. Another suitable porous inorganic carrier is
perlite which is known as the eutectic between
ferrite and cemetite and has a laminar structure
resembling mother-of-pearl, barely resolvable under
20 the finest microscopes, and occurs in steel as a
result of the transformation of austenite into
aggregations of ferrite and cementite. Perlite is
commercially available, and in actual practice may
be obtained from Borget Brothers, Santa Monica,
25 California.

Zinc oxide (ZnO) is another carrier con-
templated by the present invention. Zinc oxide is a
coarse white or grayish powder which is odorless and
has a density of 5.47 g/cm³ and a melting point of
30 1975°C. Zinc oxide is commercially available and in
actual practice may be obtained from TRI-ESS Sci-
ences, Burbank, California.

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1 Th composition hereof may include a
portion of hollow, SiO_2 glass spheres of a con-
trolled particle size and density. The spheres are
5 preferably 0.60 grams per cubic centimeter in den-
sity and average 65 to 75 microns in diameter. The
hollow spheres act as microscopic bearings with a
minimum ratio of surface area to volume, thereby
reducing viscous drag, resisting abrasion to the
10 surface and providing improved flow properties. The
hollow spheres comprise .20% by volume of the poly-
amide coating, and may be provided with a copper
coating when, for example, the composition hereof
includes a portion of cuprous oxide or other copper-
based antifoulant. The glass spheres are available
15 commercially, and in actual practice may be obtained
from the 3-M company of St. Paul, Minnesota under
the name "Glass Bubbles.", either with or without a
copper coating.

 In preferred production procedures, the
20 powdered compositions in accordance with the inven-
tion are prepared by thoroughly mixing respective
powdered amounts of the polyamide, the porous inor-
ganic carrier, and the antifoulant. Preferably, the
powder is prepared by mixing respective amounts of
25 agglomerates of carbon black and tributyltin flour-
ide in a Hobart Blender at 3600 RPM for 2 minutes,
homogenizing this mixture into powder of a size of
approximately 325 Mesh (120 microns), and then
mixing respective amounts of these pellets, Nylon 11
and glass spheres.

30 In another aspect of the invention, compo-
sitions are provided including relatively large
quantities of antifoulant such as elemental tin or
copper or cuprous oxide, and a polyamide such as
Nylon 10, 11, or 12-12. Such compositions also
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1 normally include minor amounts of adhesive and
algicid . Thus, a preferred composition may
include from about 54%-82% by weight of elemental
5 tin or copper (most preferably about 82% by weight)
of a particle size preferably less than 49 microns,
about 4-8% of an adhesive (advantageously about 4%
by weight of a nylon terpolymer/caprolactam adhesive
sold under the designation "M548" by Atochem, Inc.
10 of Birdsboro, Pennsylvania) of a particle size
preferably less than 150 microns, from about 4-8%
of an algicide (preferably about 4% by weight of a
material sold under the designation "VANCIDE 89"
by the R.T. Vanderbilt Company, Inc. of Norwalk,
15 Connecticut, which is N-trichloromethylthio-4-
cyclohexene-1,2-dicarboximide) of a particle size
preferably of 5 microns or less, and with the
balance being Nylon 11 or alternatively, Nylon 12-12
20 manufactured by E.I. DuPont de Nemours and Company
of Wilmington, Delaware. The Nylon 11 or other
polyamide preferably is of a particle size of 150
microns or less. This preferred composition has
been found to be extremely effective, and is par-
ticularly advantageous from an ecological standpoint
25 in that it has a leach rate of less than 1 microgram
of antifoulant per square millimeter per day.
Furthermore, use of elemental tin or copper avoids
the handling problems inherent in the use of tri-
butyltin antifoulants.

Other compositions within the ambit of the
invention may include from about 40 to 70% by weight
30 cuprous oxide (preferably about 52% by weight, about
4-8% by weight of adhesive (preferably about 4% by
weight of nylon terpolymer adhesive), about 8% by
weight of the "VANCIDE 89" material, and with the

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1 balance being either Nylon 10, Nylon 11, Nylon
12-12, or mixtures thereof.

5 Here again, the above-described compositions are prepared by mixing the metallic anti-foulant, adhesive and algicide in a conventional blender, such as a Hobart blender. Such powdered particles are then blended for two to three minutes at 3600 r.p.m.'s with the polyamide to provide the final coating composition which, after blending, has
10 preferably a mesh size of about 44 microns.

Preferred techniques for applying the coating compositions of the present invention include the steps of providing a high velocity flow (i.e., about Mach I or above) of a gas such as pure
15 argon; passing the gas transversely through an elongated high wattage electric arc for heating the gas and converting a portion thereof to the plasma state; injecting the powdered coating composition into the gas downstream from the arc for melting the powder without overheating the powder; directing the
20 flow of the composition and associated gas into substantially one direction for minimizing overspray and misting of the composition; and spraying said melted composition onto a surface to be coated. More preferably, the powdered composition is injected
25 into the gas stream in a downstream direction and at an angle of from about 12 to 20° to the direction of flow of the stream; and most preferably the powdered composition is injected in a downstream direction and at an angle of about 18° to that of
30 the direction of travel of the gas stream so as to minimize vortex formation within the stream and minimize the over spray associated with vortex formation. Also more preferably, the powder is injected at a distance of from about 6 to 10 inches
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1 downstream from the arc (the arc being defined as a
point of energy transfer between an anode and a
cathode) so as to minimize overheating of the com-
position and so as to ensure that the composition
5 reaches maximum velocity for a corresponding maximum
bond strength with the surface to be coated; and
more preferably, injecting the composition into the
gas stream at a location of from about 5 to 8 inches
downstream from the arc so as to achieve the proper
10 molten state of the composition and a particle
velocity favoring interatomic bonding of the compos-
ition with the surface to be coated.

If injection of the powdered composition
is made either through a high wattage arc or closely
15 adjacent thereto, the composition will be overheated
and rendered useless. If a lower wattage arc is
employed so as to generate a temperature low enough
to permit injection of the powder either through the
arc or adjacent thereto, then the application rate
20 permitted by the arc will be so low as to make large
scale application economically infeasible. Thus,
injection of the powdered composition substantially
downstream from the arc is advantageous to achieve
an economically feasible, high volumetric rate
application technique. Also, injection of the
25 powder downstream from the arc permits increased arc
temperature, which in turn permits adequate heating
of increased flows of gas thereby permitting ade-
quate melting and particle velocity for increased
powder flow rates.

30 Plasma spraying has been used in the past
in the context of spraying either ceramics or pow-
dered metals but such materials do not have the
temperature limitations of polyamide coatings. The
present invention represents applying powdered
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1 polyamide compositions involving injection of the
powder at a sufficient distance downstream from the
arc so as to achieve for the first time, high volumetric application rates of polyamide coatings.
5

The arc used in the method of the present invention has a preferred power level of 20 to 40 kilowatts and an associated gas temperature at the arc of approximately 12,000 to 30,000°F. The gas is then cooled so that by the time the gas has reached the inlet for the powdered composition, the temperature of the gas has dropped down to approximately 250 to 800°F while travelling at a speed of 5,000 to 7,000 feet per second. Gases useful in this invention include N₂, H₂, He, Ar and combinations thereof. The coatings made from the composition of the present invention when applied using the application techniques of the present invention provide coatings having application rates, densities and bond strengths substantially greater than that of coatings applied by conventional polyamide application techniques such as fluidized bed dipping, acetylene flame spraying and electrostatic spraying.
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The plasma spray method of the present invention further involves vacuuming toxic fumes from a periphery of the stream adjacent the surface to be sprayed for minimizing the escape of toxic fumes generated during heating of the composition, into the atmosphere. Vacuumed gases are oil filtered to remove the toxic gas fumes and organic acid vapors. The vacuum preferably pulls at a rate of at least 10 inches of water at 85 and preferably 360 cubic feet per minute.
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In coating a marine surface such as an aluminum boat hull, the hull may be treated in a stepwise fashion. That is, the hull may first be
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1 precoat as set forth hereinabove by injecting a
powdered polyamide selected from the group of Nylon
10 and Nylon 11 into the heated gas stream to melt
5 the polyamide. The polyamide thus melted is then
applied to the hull by directing the heated gas
stream toward the surface of the hull. The poly-
amide coating thus applied is permitted to melt to
form a precoat. The polyamide precoat is then
10 sprayed with an antifoulant coating mixture
including an antifoulant and a polyamide such as
Nylon 10 or Nylon 11. The antifoulant coating
mixture is similarly injected into a gas stream
which has passed through an electric arc thereby
15 melting the antifoulant mixture. The melted anti-
foulant coating mixture is then applied over the
precoat and allowed to cool therein, producing a
final antifoulant coating on the aluminum hull.

A skid resistant coating may also be
applied according to the method disclosed herein.
20 The coating includes respective amounts of Nylon 10
or Nylon 11, or combinations thereof, and a portion
of solid particles of aluminum oxide, which are not
melted during the injection of the compositions in
the heated gas stream.

25 The following example sets the preferred
preparation of a powdered composition in accordance
with the present invention, together with typical
steps involved in application of the coating.

EXAMPLE

30 A premelt powdered coating composition is
prepared by mixing 6 pounds of carbon black with 12
pounds of tributyltin fluoride in a Hobart Blender
at 3600 RPM for 2 minutes. This serves to blend and
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1 h mogeniz the mixture into p wdered particles of a
size f approximately 325 mesh (120 microns). Such
powdered particles are then mixed with 82 pounds of
5 powdered Nylon 11 for two to three minutes at about
3,600 r.p.m.'s.

A directed stream of pure argon gas, at a
flow rate of 1.42 cubic feet per minute (CFM) at 50
psi, is passed transversely through an electric arc
having a power level of 12 kilowatts. The arc
10 substantially heats the gas and causes some of the
gas to be converted to the plasma state. This
heated stream is then cooled as it moves away from
the arc. The powdered composition mixture is then
injected by use of a pressurized carrier gas into
15 the heated gas stream at a location of about 8.5
inches downstream from the arc and in a downstream
direction and at an angle of about 18° to that of
the general flow of the gas stream. The mixture and
the heated gas then combine to properly melt the
20 mixture and impart a substantial velocity onto the
melted mixture. The gas and mixture then are passed
further downstream together in a substantially
uniform direction so as to minimize overspray and
are then sprayed directly onto a marine surface so
25 as to form a film coating of the composition there-
on. The film coating is then allowed to cool and
bond with the surface.

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Claims

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1. A polyamide powdered mixture comprising an amount of a polyamide powder selected from the group consisting of Nylon 11, Nylon 10, and combinations thereof; and an amount of an antifoulant, said mixture, upon melting, application to a marine surface and cooling thereon, providing a low friction, growth resistant, non-abrading coating.

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2. The mixture of Claim 1, said antifoulant being selected from the group consisting of tin-based antifoulants and copper-based antifoulants.

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3. The mixture of Claim 2, said mixture further comprising porous inorganic carrier.

20

4. The mixture of Claim 3, said mixture further comprising a portion of SiO₂ glass spheres.

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5. A polyamide, powdered mixture comprising an amount of a polyamide powder selected from the group consisting of Nylon 11, Nylon 10, and combinations thereof; an amount of an inorganic porous carrier; and an amount of a tin based antifoulant, said mixture, upon melting, application to a marine surface and cooling thereon, providing a low friction, growth resistant, non-abrading coating, said antifoulant being released from said coating into the marine environment at a rate of less than 5 micrograms per square millimeter of coating surface per day.

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6. The mixture of Claim 5, said antifoulant being tributyltin fluoride.

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7. The mixture of Claim 5, said inorganic carrier being carbon black.

8. The mixture of Claim 5, said polyamide being Nylon 11.

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9. The mixture of Claim 5:

said polyamide being present at a level of from about 45 to 60% by weight;

said inorganic carrier being present at a level from about 15 to 18% by weight; and

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said antifoulant being present at a level from about 25 to 37% by weight.

10. The mixture of Claim 4, said mixture further comprising a portion of SiO_2 glass spheres.

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11. The mixture of Claim 10: said glass spheres being present at a level of .20% by volume.

12. A powdered, coating mixture comprising:

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from about 63 to 82% by weight of Nylon 11;

from about 6 to 12% by weight of carbon black; and

from about 12 to 25% by weight of tributyltin fluoride.

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13. A polyamide, powdered mixture comprising an amount of a polyamide powder selected from the group consisting of Nylon 11, Nylon 10, and combinations thereof; and an amount of a copper based antifoulant, said mixture, upon melting and application to a marine surface and cooling thereon, providing a low friction, growth resistant, non-abrading coating thereon.

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10 14. The mixture of Claim 13, said antifoulant being selected from the group consisting of elemental copper and cuprous oxide.

15 15. The mixture of Claim 14, said mixture further comprising a portion of SiO₂, glass spheres, said spheres being provided with a copper coating.

20 16. A method of applying a protective coating to a marine surfaces comprising the steps of:

providing an electric arc;
directing a high velocity gas stream through said arc thereby heating said gas stream;
injecting a powdered mixture into said heated gas stream, said powdered mixture comprising an amount of a polyamide selected from the group consisting of Nylon 11, Nylon 10, and combinations thereof; and an amount of an antifoulant, at a location substantially downstream from said arc whereby to melt said powdered mixture without overheating said powdered mixture; and
applying said melted mixture to said surface.

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17. The method of Claim 16, wherein said powdered mixture includes a quantity of an inorganic porous carrier.

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18. The method of Claim 17, wherein said inorganic porous carrier is carbon black.

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19. The method of Claim 16, wherein said gas is selected from a group consisting of Ar, N₂, H₂, He and combinations thereof.

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20. The method of Claim 16, wherein the flow of said gas and said powdered mixture are directed in a substantially uniform direction following injection of said powdered mixture into said gas stream.

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21. The method of Claim 16, wherein said arc has a power level of 20 to 40 kilowatts.

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22. The method of Claim 16, wherein said gas stream is heated to a temperature of about 12,000 to 30,000°F.

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23. The method of Claim 16, wherein said melted mixture reaches a maximum temperature of from about 250 to 800°F.

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24. A method of coating a marine surface, comprising the steps of precoating said surface with a polyamide selected from the group consisting of Nylon 10 and Nylon 11, said precoating including the steps of melting said polyamide, applying said melted polyamide to said surface and allowing said melted polyamide to cool thereon thereby forming a precoat; and coating said precoat with a mixture comprising an amount of a polyamide powder, selected from the group consisting of Nylon 10, Nylon 11, and mixtures thereof, and an amount of an antifoulant, said coating including the steps of melting said mixture, applying said melted mixture to said precoat and allowing said melted mixture to cool thereon.

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25. A skid resistant coating comprising respective amounts of a polyamide selected from the group consisting of Nylon 11, Nylon 10, and combinations thereof; and solid particles of aluminum oxide.

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26. The mixture of Claim 1, said antifoulant being selected from the group consisting of elemental tin, elemental copper and mixtures thereof.

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27. The mixture of Claim 26, said antifoulant being present at a level of from about 72% by weight up to the amount thereof which would render the mixture effectively electrically conductive.

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28. The mixture of Claim 26, including an amount of a synthetic resin adhesive.

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29. The mixture of Claim 28, said adhesive comprising a nylon terpolymer based adhesive and being present at a level of from about 4% to 8% by weight in said composition.

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30. The mixture of Claim 26, including an amount of an algicide.

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INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US89/02056**

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC(4): C08L 77/02; C08K 3/22; B05D 3/06 US. CL: 523/122; 427/37; 524/430								
II. FIELDS SEARCHED <div style="text-align: right; font-size: small;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border: 1px solid black; padding: 5px;">Classification System</td> <td style="border: none;"></td> <td style="width: 70%; border: none;"></td> </tr> <tr> <td style="border: 1px solid black; text-align: center; padding: 10px;">US</td> <td style="border: none;"></td> <td style="border: 1px solid black; padding: 10px;"> 523/122, 606 427/37 524/430 </td> </tr> </table> <div style="text-align: center; font-size: x-small; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸</div>			Classification System			US		523/122, 606 427/37 524/430
Classification System								
US		523/122, 606 427/37 524/430						
III. DOCUMENTS CONSIDERED TO BE RELEVANT *								
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³						
X	US, A, 3,988,287 (INOKUCHI) 26 OCTOBER 1976. SEE COL. 1, LINES 54-65;	25						
X	US, A, 3,833,534 (TIERNEY ET AL) 03 SEPTEMBER 1974. SEE COL. 3, LINES 54-64; COL. 6, LINES 43-45 AND 56-63.	25						
Y	US, A, 4,689,364 (MUMCU ET AL) 25 AUGUST 1987. SEE COL. 3, LINES 35-51; COL. 4, LINES 19-30.	1-8, 10						
Y	US, A, 3,861,949 (ONOZUKA ET AL) 21 JANUARY 1975. SEE COL. 2, LINES 31-50, COL. 7, LINES 60-68 AND COL. 8, LINES 1-15.	1-8, 10						
Y	GB, A, 2,099,444 (JENSON ET AL) 08 DECEMBER 1982. SEE PAGE 1, LINES 60-64; PAGE 2, LINES 9-16.	1-8, 10						
A	US, A, 3,947,607 (GAZZARD ET AL) 30 MARCH 1976. SEE ENTIRE DOCUMENT.	11-24						
A	US, A, 4,197,233 (MARSHALL) 08 APRIL 1980. SEE ENTIRE DOCUMENT.	26-30						
<div style="display: flex; justify-content: space-between; font-size: x-small;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>								
IV. CERTIFICATION								
Date of the Actual Completion of the International Search 30 AUGUST 1989		Date of Mailing of this International Search Report <div style="text-align: center; font-size: large; font-weight: bold;">28 SEP 1989</div>						
International Searching Authority ISA/US		Signature of Authorized Officer <div style="text-align: center;"> L. T. JACOBS </div>						

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4,410,642 (LAYTON) 18 OCTOBER 1983. SEE ENTIRE DOCUMENT.	26-30
A	US, A, 4,701,518 (OSBORN ET AL) 20 OCTOBER 1987. SEE ABSTRACT.	30